EUR 3914 e
Part I

EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

HIGH DOSE INTEGRATING CHEMICAL DOSIMETERS

The radiolysis of aqueous sodium formate solutions

by

G. JUPPE, H. KOLMAR and R. FANTECHI

1968

Joint Nuclear Research Center
Ispra Establishment - Italy

Chemistry Department
Organic Chemistry

LEGAL NOTICE

This report is on sale at the addresses listed on cover page 4

at the price of FF 5.—	FB 50.—	DM 4.—	Lit. 620	Fl. 3.60

When ordering, please quote the EUR number and the title, which are indicated on the cover of each report.

Printed by Guyot, s.a.
Brussels, May 1968

EUR 3914 e
Part I

EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

HIGH DOSE INTEGRATING CHEMICAL DOSIMETERS

The radiolysis of aqueous sodium formate solutions

by

G. JUPPE, H. KOLMAR and R. FANTECHI

1968

Joint Nuclear Research Center
Ispra Establishment - Italy

Chemistry Department
Organic Chemistry

SUMMARY

The fast electron radiolysis of aqueous sodium formate solutions was studied. For a 0.1 N solution a zero order kinetics was observed for the decrease in formate up to 83 % conversion ($k = 5 \times 10^{-4} mEq ml^{-1} sec^{-1}$). For the destruction of secondary radiolysis products, oxidizable by permanganate in acid solution, a first order kinetics was found ($k = 6.7 \times 10^{-4} sec^{-1}$). The 0.5 N solution showed linearity between total dose and reductant formation only up to appr. 30 % conversion of the starting material.

The permanganate titration of reductants in acid and alkaline solution and the acid base titration of total and free hydroxide led to the assignment of the following initial G-values for 0.5 N solutions :

$G_{\text{permanganate oxidizable compounds in acid solution}} = + 3.26$

$G_{\text{permanganate oxidizable compounds in alkaline solution}} = - 3.16$

$G_{\text{free hydroxide}} = + 0.5$

$G_{\text{total hydroxide}} = + 1.2$

$G_{\text{formate}} = - 3.3$

$G_{\text{oxalate}} = + 2.2$

$G_{\text{carboxy groups}} = - 1.2$

$G_{\text{neutral functions from carboxy groups}} = + 0.8$

KEYWORDS

RADIOLYSIS
WATER
SOLUTIONS
SODIUM COMPOUNDS
FORMIC ACID
REACTION KINETICS

G-value, titration, permanganates

CONTENTS

HIGH DOSE INTEGRATING CHEMICAL DOSIMETERS
The Radiolysis of Aqueous Sodium Formate Solutions(+)

Aqueous solutions of sodium formate have been proposed for use as high dose integrating chemical dosimeters[1]. Though this system has never been tested for in pile monitoring it has successfully been tried for light particle irradiation. The useful range was then 1 to 8o x 1o^6 rad. The oxidizable products formed during the irradiation were conveniently analyzed by acidic permanganate titration. Due to the neutral solution no corrosion appeared in the metallic vessels. A linear response of reductant formation versus energy absorption was found up to at least 8o% destruction of the starting material. This high dose integrating capacity makes this system interesting also for in-pile dosimetry. In this case the sodium formate should be replaced by formic acid to avoid neutron activation of the cation.

Only very little is known about the mechanism of the radiolytic decomposition. In the present investigation the kinetics of the radiolysis of aqueous sodium formate solutions were studied. Our aim was to gain information about the reaction products and to elucidate the individual steps of the mechanism, being responsible for their formation.

1. - I N T R O D U C T I O N

H.Fricke and E.Hart[2] studied more than 2o years ago the X-ray radiolysis of aqueous formic acid solutions. For oxygen-free solutions at pH 3 or below the product stoichiometry could be represented in terms of the net reaction:

(+)Manuscript received on March 1, 1968.

$$HCOOH \xrightarrow{\sim\sim} H_2 + CO_2 \qquad (1)$$

Equal amounts of these gases were formed over the concentration range o.oo1 to o.o5 M. Above o.o5 M the yield of carbon dioxide increased, whereas the hydrogen yield remained essentially constant. The authors suggested that an additional overall reaction may be involved at the higher formic acid concentrations. The existence of a chain reaction was postulated but no evidence as to its exact nature could be procured.

E.J.Hart[3] showed in a later investigation that the oxidation of formic acid, initiated by gamma irradiation of its aqueous solution, occured as a result of its reaction with the H and OH radicals, being produced by the primary ionisation of the aqueous solvent[+]. The existence of a chain reaction was inferred in which hydroxyl and hydrogen radicals attack formic acid to produce HCOO radicals:

[+] The quantitative features of the ionization processes occurring when Compton recoil electrons interact with water can be summarized by the following equations leading as net reaction to the formation of hydrogen and hydroxyl radicals (4)

$$H_2O + e_c \longrightarrow H_2O^+ + e_{c1} + e_s$$

$$H_2O + e_{cn} \longrightarrow H_2O^+ + e_{c,n+1} + e_s$$

$$H_2O + e_s \longrightarrow H_2O^+ + e_{s1} + e_s$$

$$H_2O + e_{sn} \longrightarrow H_2O + e_{s,n+1} + e_s$$

$$(H_2O^+)aq \longrightarrow H_3O^+aq + OH$$

$$H_2O + e_s (\text{or } e_{sn}) \longrightarrow H + OH^-(aq)$$

Where e_c = Compton recoil electron, e_{cn} = Compton recoil electron after the n^{th} ionization, e_s = secondary electron, e_{sn} = sec. electron after the n^{th} ionization.

$$OH^{\bullet} + HCOOH \longrightarrow H_2O + HCOO^{\bullet} \text{ (or } {}^{\bullet}COOH) \quad (2)$$

$$H^{\bullet} + HCOOH \longrightarrow H_2 + HCOO^{\bullet} \quad (3)$$

$${}^{\bullet}COOH + H_2O_2 \longrightarrow H_2O + CO_2 + OH^{\bullet} \quad (4)$$

Radical removal was assumed to occur via:

$$H^{\bullet} + {}^{\bullet}COOH \longrightarrow H_2 + CO_2 \quad (5)$$

$$OH^{\bullet} + {}^{\bullet}COOH \longrightarrow H_2O + CO_2 \quad (6)$$

Hydrogen peroxide, which is formed as a radiolysis product from pure water, was not detected as final reaction product when irradiating aqueous formic acid solutions.

E.J.Hart[5] investigated the kinetics of the radiolytic decomposition of formic acid solutions after adding hydrogen peroxide. Carbon dioxide formation increased with increasing initial hydrogen peroxide concentration; oxygen consumption was found to be independent of peroxide concentration.

Oxygen is a powerful inhibitor in the radiation induced chain decomposition of formic acid - hxdrogen peroxide solutions. E.J.Hart[5] measured the radiation yields of carbon dioxide, hydrogen and hydrogen peroxide formed and oxygen reacted over the formic acid concentration range $1o^{-4}$ to 1.o M and the oxygen concentration range from 5 x $1o^{-3}$ to 1.2 mM. All experiments were done at pH from 1.7 to 3.o. The addition of oxygen resulted in a decrease of hydrogen production. The oxygen consumption was practically constant all over the range of HCOOH concentrations studied ($1o^{-4}$ to 1 M).

A mechanism capable of accounting for the behaviour of formic acid - oxygen solutions in the concentration range 5 to 5o mM HCOOH was given by Hart as follows:

H_2O	$\rightsquigarrow$	$H + OH$	k_7	(7)
H_2O	$\rightsquigarrow$	$\frac{1}{2} H_2 + \frac{1}{2} H_2O_2$	k_8	(8)
$OH + HCOOH$	$\dashrightarrow$	$H_2O + HCOO$	k_9	(9)
$H + HCOOH$	$\dashrightarrow$	$H_2 + HCOO$	k_{10}	(10)
$HCOO + O_2$	$\dashrightarrow$	$HO_2 + CO_2$	k_{11}	(11)
$HCOO + H_2O_2$	$\dashrightarrow$	$H_2O + CO_2 + OH$	k_{12}	(12)
$H + O_2$	$\dashrightarrow$	HO_2	k_{13}	(13)
$HO_2 + HO_2$	$\dashrightarrow$	$H_2O_2 + O_2$	k_{14}	(14)

The yields of products as functions of oxygen, hydrogen peroxide and formic acid concentration are given by the following expressions, derived from the assumed mechanism and assuming that a steady state between intermediate free radicals (H, OH, HO_2, HCOO) is readily established:

$$G(CO_2) = \left[G(7) + \frac{G(7)}{1 + k_{13}(O_2)/k_{10}(HCOOH)}\right] \times \left[1 + k_{12}(H_2O_2)/k_{11}(O_2)\right]$$

$$G(-O_2) = G(7)$$

$$G(H_2) = \frac{G(8)}{2} + \frac{G(7)}{1 + k_{13}(O_2)/k_{10}(HCOOH)}$$

$$G(H_2O_2) = G(7) + \frac{G(8)}{2} - G(7)\,\frac{k_{12}(H_2O_2)}{k_{11}(O_2)}\left[1 + \frac{1}{1 + k_{13}(O_2)/k_{10}(HCOOH)}\right]$$

In a more recent work E.J.Hart[6] examined the effect of pH on the yields of free radicals and molecular products for aqueous formic acid - oxygen solutions. In the range of pH 2,7 to 11,6 the formation of carbon dioxide, hydrogen and hydrogen peroxide was found independent of pH. However, in the acid range below pH 2,7 hydrogen peroxide formation and oxygen consumption rose perceptibly above the averages for the higher pH's. Carbon dioxide and hydrogen production, however, were decreasing in acid solution.

W.M.Garrison, W.Bennett and S.Cole[7] bombarded aqueous ^{14}C-formic acid solutions with high energy helium ions from a cyclotron and detected the production of glyoxylic, oxalic, glycolic, tartronic, mesoxalic acid together with small amounts of tartaric acid and formaldehyde. These compounds were obtained at radiation doses which corresponded to the removal of less than one percent of the formic acid initially present in the target solution. The formation of glyoxylic acid and glyoxal was accounted for assuming a H-addition to formic acid:

$$H + HCOOH \longrightarrow HC\begin{matrix}\diagup OH \\ \diagdown OH\end{matrix}$$

This radical could then combine with a COOH-radical to give glyoxylic acid ($HC(OH)_2 + COOH \longrightarrow CHOCOOH + H_2O$) or dimerize to form glyoxal. This reaction was claimed to appear only at the very high radical concentration in cyclotron irradiations and not likely to appear at low LET gamma-, fast electron- or X-irradiations.

The formation of oxalic acid was not observed in neutron irradiation of o.25 M oxalic acid. Its observed formation in the high-dose irradiation with charged particles (high LET) was explained as a dimerization of the COOH radical:

$$2\ COOH \longrightarrow (COOH)_2 \qquad (15)$$

while in neutron irradiation (low LET) the following reaction should prevail:

$$COOH + HCOOH \longrightarrow HCOOH + HCOO \qquad (16)$$

The formation of the other compounds in charged-particle irradiation was accounted for by the following reactions:

$$H + HCOOH \rightleftharpoons HC(OH)_2 \qquad (17)$$

$$HC(OH)_2 + COOH \longrightarrow CHOCOOH + H_2O \qquad (18)$$

$$2\ HC(OH)_2 \longrightarrow \begin{matrix} CHO \\ | \\ CHO \end{matrix} + 2H_2O \qquad (18a)$$

$$CHOCOOH + H \longrightarrow CHOHCOOH \qquad (19)$$

$$CHOHCOOH + COOH \longrightarrow CH_2OHCOOH + CO_2 \qquad (2o)$$

$$CHOHCOOH + COOH \longrightarrow CHOH(COOH)_2 \qquad (21)$$

$$2\ CHOHCOOH \longrightarrow (CHOHCOOH)_2 \qquad (22)$$

$$(COOH)_2 + H \longrightarrow COCOOH + H_2O \qquad (23)$$

$$COCOOH + COOH \longrightarrow CO(COOH)_2 \qquad (24)$$

For o.25 N HCOOH solutions irradiated with 4o MeV helium ions the same authors found the following G-values:

oxalic acid:	o.o82 - o.11
glyoxylic acid:	o.18 - o.23
glycolic acid:	o.o14 - o.o3
mesoxalic acid:	o.11 - o.2o
tartronic acid:	o.o35 - o.o45
tartaric acid:	$\sim$ o.oo4 - o.oo6
formaldehyde:	$<$ o.oo5

An explanation of the pH-effects in the radiolysis of aquo-formic acid systems was given by E.Hayon and J.Weiss[8]. These authors proposed that the marked pH-dependence of hydrogen yields in the radiolysis of air-free solutions of organic compounds was consistent with the following reactions:

$$H_2O \longrightarrow H_2O^+ + e^- \quad (25)$$

$$e^- + H_2O \longrightarrow H_2O^- \text{ (solvated electron)} \quad (26)$$

$$H^+ + H_2O^- \longrightarrow H + H_2O \quad (27)$$

$$H + RH \longrightarrow H_2 + R \quad (28)$$

The two last mentioned reactions would explain the higher G-value for the hydrogen formation in strongly acidic medium, originating from the oxalic acid molecules. At higher pH-values reactions (27) and hence (28) become less important and a competing reaction was suggested as being responsible for the removal of the solvated electron

$$2\ H_2O^- \longrightarrow H_2 + 2\ OH^- \quad (29)$$

T.J.Hardwick[1] investigated the radiolysis of formate in alkaline solution by irradiating sodium formate with fast electrons. The formation of products titratable with permanganate in acid solution was found linear with energy absorbed to at least 80% of complete reaction. The yield (G) was found to be about 3.40 molecular equivalents per 100 eV absorbed. No effect of formate concentration was noted in the range 0.05 to 0.30 M[+]. In the temperature range 0°C to 40°C no

---

[+] I.Janovsky, B.Bartonicek and J.Bednar[9] found, that gamma irradiation gives a lower G-value, and that this is strongly dependent from the initial formate concentration (2,6 at 0,08 M/l; 3,0 at 0,3 M/l; 3,4 at 1 M/l).

difference in reductant yield due to temperature effects was observed. Possible effects due to oxygen present in the solution from dissolved air were not measurable. When oxygen was bubbled continuously through the system during irradiation, nevertheless, erratic results were found. This was attributed to the formation of hydrogen peroxide which may catalytically decompose and/or scavenge radicals. No dose-rate effect was noted. The pH of the sodium formate solution, being about 7,5 at the beginning of the irradiation, rose rapidly to 1o to 11 and remained then constant.

T.Hardwick[1o] investigated also the product formation from the radiolysis of aqueous sodium formate solutions by fast electrons. The following G-values were found or calculated from experimental data: oxalate: G = 1,35; hydrogen: G = 1,18; glyoxalate: G = o,64. These values were nearly the same as found in the neutron irradiation of sodium formate solution by W.M.Garrison, W.Bennett and S.Cole[7]: oxalate: G = 1,2; glyoxalate: G = o,8o. T.Hardwick postulated the following kinetic scheme from which the yield of each reaction could be calculated from the measured yields of sodium oxalate, hydrogen and excess alkali:

$$\cdot COOH + COOH \longrightarrow (COOH)_2 \quad (G = 1,35) \quad (3o)$$

$$\cdot COOH + HC(OH)_2 \longrightarrow 2\ HCOOH \quad (G = o,1) \quad (31)$$

$$\longrightarrow CHO\text{-}COOH + H_2O \quad (G = o,64) \quad (32)$$

$$\cdot H + HC(OH)_2 \longrightarrow H_2 + HCOOH \quad (G = o,77) \quad (33)$$

$$\longrightarrow H_2O + HCHO \quad (G = o,17) \quad (34)$$

2. - MATERIALS AND METHODS

2.1 - MATERIALS

All chemicals used were analytical grade. Water was distilled from alkaline permanganate and redistilled in a quartz apparatus. The solutions of sodium formate had been purged with nitrogen before the irradiations.

2.2 - SOURCE OF RADIATION

The source of radiation was a Van de Graaff electron accelerator of 2 MeV, 250 μA capacity (High Voltage Engineering Corporation, Amersfoort, Holland). In all our experiments a current of 120 μA and a voltage setting of 1,5 MeV were used giving an unfocussed spot beam having a diameter of app. 8 mm when hitting the window of the irradiation cell.

2.3 - IRRADIATION CELL

The stainless steel irradiation cell is shown in fig. 1. It contained 50 ml of solution which could be kept at a constant temperature by pumping water through the cooling mantle from a thermostat. The removable window was 0.20 mm thick and could withstand pressures of more than 60 atm. For normal work a rotating stainless steel stirrer through the upper tube of the vessel was used. The vessel was cooled by a stream of water. For more precise work in order to obtain a rigorous control of the temperature, the following system has also been developed. Opposite the window inside the radiation

cell was fitted a teflon support bearing a glass-enclosed magnet, which was free to rotate in a vertical plane. The speed of the internal magnetic stirrer was 1200 rpm which was calculated from the signals observed on an oscilloscope screen. These were formed by the induction of a small current in a coil on the outer side of the irradiation vessel, by a small magnet fixed to the rotating propeller inside the vessel. The irradiation cell was screwed directly to the outer end of the accelerator tube to ensure reproducible geometry for the experiments and a minimum distance for the electrons before hitting the samples.

2.4 - TEMPERATURE CONTROL OF THE IRRADIATION VESSEL

The electronic set-up described in fig. 2 allowed to keep the temperature in the irradiation vessels constant within ± 0,5°C. The temperature of the irradiated liquid was measured on a recording potentiometer via a thermoelement placed in the irradiation cell. This value was constantly compared on a potentiometer with a value preselected for the experiment. Depending on the deviation of these two temperature readings, an electromagnetic valve allowed or stopped the water flow from the thermostat thus controlling its heating or cooling action and compensating for the heat evolved by the irradiation.

2.5 - ANALYSIS OF THE REACTION PRODUCTS

2.5.1 - PERMANGANATE TITRATION OF REDUCTANTS IN ACIDIC SOLUTION

One to five ml of reactant were made 2 N in sulfuric acid after irradiation. They were then titrated with o,1 N potassium permanganate at a temperature between 8o°C and 9o°C. Starting formate was not oxydized under these conditions. Aqueous solutions of pure oxalic acid gave sharp end points under these conditions of the titration. This was not observed when titrating the radiolyzed solution. We titrated therefore the reaction solution up to a point where the permanganate colour remained for at least 1o seconds (1^{st} R_a-value). The titration was then continued until the permanganate was not decolorized for more than 12o seconds (2^{nd} R_a-value). The difference between these two values gave a rough estimation for the formation of reducing reaction products other than oxalic acid.

These R_a-values were reproducible at titration temperatures between 8o°C and 9o°C.

2.5.2 - PERMANGANATE TITRATION OF REDUCTANTS IN ALKALINE SOLUTION

The titration with permanganate in alkaline solution leads to the determination of oxalate and other acid ions, including residual formate, being oxidized under these conditions.

One to five ml of the irradiated solution were saturated with sodium carbonate and then oxidized with an excess of o,1 N potassium permanganate. During this operation the solution was heated for about 15 minutes to about 9o°C. Sodium oxalate was added, the solution acidified with 2 N sulfuric acid and the acid solution then titrated with potassium permanganate as described before (R_b-values).

2.5.3 - DETERMINATION OF THE TOTAL CARBOXY GROUPS HAVING DISAPPEARED DURING THE RADIOLYSIS

A first indication about the pH of the irradiated solution was obtained in the following way: to 5 ml of the sample, diluted with 5 ml of water, was added o.1 N sulfuric acid. The solution was heated, phenolphthalein as indicator added and after cooling retitrated with o.1 N sodium hydroxide.

To a sample of the irradiated solution, diluted with 5 ml water, was then added only as much o.1 N sulfuric acid that no more than o.2 ml o.1 N sodium hydroxide were consumed when retitrating the excess of the acid. By this method we avoided that formic acid was lost during the following heating of the sample for app. 5 minutes to 98°C. The sample was then retitrated with o.1 N sodium hydroxide. The values obtained (H_t-values) represent the total consumption of acid in mEq per 5o ml of solution.

2.5.4 - DETERMINATION OF CARBOXY GROUPS BEING TRANSFORMED INTO CARBON DIOXIDE AND NEUTRAL C-FUNCTIONS

A first indication about the pH of the irradiated solution after barium chloride addition was obtained in the following way: to 5 ml of the sample, diluted with 5 ml of water, was added an excess of barium chloride and phenolphthalein as indicator. If necessary o.1 N sodium hydroxide was added to make the solution alkaline. The excess hydroxide was then titrated with o.1 N sulfuric acid.

To a sample of the irradiated solution, diluted with 5 ml of water, was then added only as much o.1 N sodium hydroxide that no more than o.1 ml o.1 N sulfuric acid was consumed when retitrating with o.1 N sulfuric acid. This was only done when the pH of the irradiated sample was higher than 8.3. By this method we obtained in all cases a quantitative precipitation with barium chloride of carbonate and bicarbonate, being only possible in alkaline solution, and avoided the absorption of carbon dioxide from air appearing at a strong basicity of the solution. The solutions were titrated or retitrated with o.1 N sulfuric acid. The values obtained (H_f-values in mEq/5o ml solution) represent either the direct o.1 N sulfuric acid consumption (if the initial solution had a pH higher than 8.3) or the difference between the o.1 N sodium hydroxide titration values minus the o.1 N sulfuric acid values (if the initial solution had a pH lower than 8.3). These values could be positive or negative*).

---

*) In an aqueous sodium carbonate solution addition of barium chloride leads to a neutral reaction

$$2\ NaOH + CO_2 + BaCl_2 \rightarrow BaCO_3 + 2\ Na^+ + 2\ Cl^- + H_2O$$

The free hydroxide value (H_f-value) is then zero.
A solution containing more than 2 equivalents hydroxyl anions per mole carbon dioxide remains still alkaline ($H_f > 0$), a solution containing less than 2 equivalents hydroxyl anion per mole carbon dioxide reacts acidic ($H_f < 0$).
The initial sodium formate solution is alkaline due to hydrolysis. The H_f-value is accordingly > 0. The other extreme case is the complete decomposition of sodium formate due to radiolysis:

$$H_2O + NaCOOH \rightarrow CO_2 + Na^+ + OH^- + H_2$$

This solution contains then only one hydroxyl anion per mole CO_2 formed and after $CaCl_2$-addition an acidic reaction and, accordingly, a negative H_f-value are obtained.

$$NaOH + CO_2 + BaCl_2 \rightarrow BaCO_3 + Na^+ + 2\ Cl^- + H^+$$

The initial basicity (before barium chloride addition) (H_t-value) appears now as acid reaction, i.e. $H_t = -H_f$.
In between these cases a positive or a negative H_f-value can be obtained depending on the ratio of hydroxyl anions and carbon dioxide formed.

2.6 - ISOLATION OF RADIOLYSIS PRODUCTS

2.6.1 - NEUTRAL REACTION PRODUCTS

50 ml of a 0.5 M sodium formate solution (initial formate content 25 mM; dose absorbed 150 x 10^6 rad) were ether perforated at room temperature for 90 hours. The ether was then evaporated and only a negligible amount of residue, containing neutral material, was left. The aqueous solution was then acidified and the ether perforation continued for an additional 90 hours. The ether extracted acids and the acids still contained in the aqueous solution were then determined by permanganate titration in acidic solution (R_a-values). The sum of both values compared with the initial reductant concentration before the alkaline perforation indicated that more than 98% of the reductants present were acidic products.

2.6.2 - ACIDIC PRODUCTS

We tried to separate the mixture of acids formed by partition chromatography. A glass column of 50 cm length and 20 mm internal diameter was used. 70 g silica gel (BDH) was dried for 10 hours at 105°C and then treated with 12 ml 0.5 N sulfuric acid. 100 ml chloroform saturated with 0.5 N sulfuric acid were added and the slurry filled into the column. The chloroform was removed by eluating it with ether saturated with sulfuric acid.

50 ml of the irradiated solution were perforated with ether for 25 hours. The alkaline solution was then acidified with 2 N sulfuric acid and the perforation continued for additional 72 hours. The acid mixture obtained from the ether solution was dissolved in 25 ml of water. 2 ml of this solution were vacuum dried, then dissolved in 0.4 ml 0.5 N sulfuric acid. 600 mg of silica gel were added and a slurry made with chloroform filled on top of the column.

For eluating the acids two solvents were used:
(a) water as the stationary phase, and butanol-chloroform mixtures as the mobile phase; the butanol concentration was gradually raised.
(b) o.5 N sulfuric acid as the stationary phase and ether as the mobile phase.

25 ml samples of the eluate were titrated with o.1 N sodium hydroxide.

3 - R E S U L T S

3.1 - KINETICS

3.1.1 - DEPENDENCE OF REDUCTANT FORMATION FROM THE DOSE ABSORBED

Table 1 shows the dependence of reductant formation from the total dose absorbed. The consumption of permanganate in acid solution is a direct measure for the formation of reducing reaction products formed after different radiolysis times during the irradiation with 1.5 MeV electrons. The kinetics of reductant formation are illustrated in fig. 3 and 3a) for an irradiation at 1.5 MeV and 100 /uA. Similar results for an irradiation at 1.5 MeV and 120 /uA are shown in table 1.

TABLE 1 RADIOLYSIS OF o.1 N SODIUM FORMATE (1.5 MeV, 120 /uA)
TOTAL DOSE DEPENDENCE OF REDUCTANT FORMATION

IRRADIATION TIME (sec)	TOTAL DOSE (10^6 rad)	1st R_a-VALUE (mEq/5o ml solution)
5o	8,35	1,58
1oo	16,7	3,14
15o	25	4,61
175	29,2	4,82

Table 2 lists the corresponding figures obtained after the radiolysis of a o.5 N sodium formate solution. Furthermore the 1st R_a-values (decoloring time of permanganate less than 1o seconds) and the 2nd Ra-values (decoloring time of permanganate more than 1oo seconds) of the titrations in acid solutions are compared.

TABLE 2 RADIOLYSIS OF A o.5 N SODIUM FORMATE SOLUTION
TOTAL DOSE DEPENDENCE OF REDUCTANT FORMATION

IRRADIATION TIME (sec)	TOTAL DOSE ($1o^6$ rad)	1st R_a-VALUE (mEq/5o ml solution)	2nd R_a-VALUE (mEq/5o ml solution)
15o	25	4,8o	5,15
3oo	5o	9,15	9,9o
45o	75	13,9	15,3
6oo	1oo	17,3	18,9
75o	125	2o,1	22,3
9oo	15o	21,2	23,9
1o5o	175	21,o	23,9
12oo	2oo	19,8	22,8
15oo	25o	17,15	19,4
21oo	35o	13,15	14,3

The 1st R_a-value stands for the number of oxalic acid equivalents, and the 2nd R_a-value gives a rough measure of other acids also present with the exception of formic acid which is not oxidized under these conditions.

Fig. 4 gives an example of permanganate titration leading to the 1st and 2nd R_a-values.

In table 3 the results of the oxydative titration in alkaline medium are listed. The permanganate equivalents consumed (R_b-values) are a direct measure of all reducing compounds in solution including residual formate.

TABLE 3 RADIOLYSIS OF o.5 N SODIUM FORMATE
PERMANGANATE REDUCTION IN ALKALINE MEDIUM

IRRADIATION TIME (sec)	TOTAL DOSE (10^6 rad)	R_b-VALUE (mEq/5o ml solution)
o	o	49,8
37,5	6,25	-
15o	25,o	44,25
3oo	5o	41,3
45o	75	37,4
6oo	1oo	34,7
75o	125	31,7
9oo	15o	29,7
1o5o	175	28,2
12oo	2oo	26,1
15oo	25o	23,2
21oo	35o	17,25

Table 4 shows the reproducibility of the manganometric titrations in both acid and alkaline medium. Different samples irradiated at different times are here compared.

TABLE 4 REPRODUCIBILITY OF MANGANOMETRIC TITRATIONS

IRRADIATION TIME (sec)	mEq/5o ml solution		
	1st R_a-VALUE	2nd R_a-VALUE	R_b-VALUE
9oo	21,1	23,7	31,5
9oo	21,2	23,7	31,2
9oo	21,o	23,9	29,7

Fig. 5 summarizes graphically the results of the acid and alkaline titrations. Both the 1st and 2nd R_a-values, and the R_b-values are plotted against irradiation time, i.e. total dose absorbed by an initially o.5 N sodium formate solution.

3.1.2 - DEPENDENCE OF CONCENTRATION OF ACIDS FROM THE DOSE ABSORBED

The results of the titrations of the irradiated samples with or without previous precipitation of carbonate by $BaCl_2$-addition are listed in table 5 and graphically illustrated in fig. 6. The meaning of H_t and H_f has been explained in chapter 2.5.3 and 2.5.4.

TABLE 5 RADIOLYSIS OF o.5 N SODIUM FORMATE
ACID-BASE TITRATIONS

IRRADIATION TIME (sec)	TOTAL DOSE (10^6 rad)	FREE HYDROXIDE H_f (mEq/5o ml solution)	TOTAL HYDROXIDE H_t (mEq/5o ml solution)
37,5	6,25	o,15	o,31
15o	25	o,8o	1,77
3oo	5o	1,45	3,48
45o	75	1,85	5,8o
6oo	1oo	2,27	7,7o
75o	125	2,68	9,3o
9oo	15o	2,5	1o,7
1o5o	175	1,85	11,5
12oo	2oo	o,4	12,o
15oo	25o	2,9	13,3
21oo	35o	9,o5	15,7

Table 6 shows the reproducibility of the acid-base titrations. Different samples are herein compared having been irradiated for different times.

TABLE 6 REPRODUCIBILITY OF ACID-BASE TITRATIONS

IRRADIATION TIME (sec)	(mEq/5o ml solution) H_f-VALUE	H_t-VALUE
9oo	2,2	1o,5
9oo	2,5	1o,7
9oo	2,3	1o,8

3.2 - SEPARATION OF ACIDS

As stationary phase of the solvent o.5 N sulfuric acid was used. Fig. 7 describes the results obtained with ether as mobile phase, fig. 8 the experiments performed with butanol - chloroform mixtures as mobile phase. Oxalic acid was isolated from the eluate of peak I, tartronic acid from peak II in fig. 7. The total dose received by the samples was in both cases appr. 18o x 10^6 rads.

4 - DISCUSSION OF THE RESULTS

4.1 - MANGANOMETRIC TITRATIONS

4.1.1 - PERMANGANATE TITRATION OF REDUCTANTS IN ACIDIC SOLUTION

The equivalents of permanganate consumed after acidifying an irradiated sodium formate solution, being o.1 N before the radiolysis, is linear with the dose absorbed up to app. 83% conversion of the starting material (fig. 3). Based on a G-value of 3.63 for the reductant formation this corresponds to an energy absorption of app. 2o x 10^6 rad. At a higher dose a levelling off of the curve is observed approaching finally a maximum after 99% total conversion of the sodium formate or after 25 x 10^6 rads energy absorption. At still higher absorptions the concentration of reductant present in the radiolyzed solution decreases. Starting from app. 27 x 10^6 rad absorption a decreasing relationship is obtained. The same manganometric titration values are thus obtained at both 21 x 10^6 and 62 x 10^6 rad total energy absorption.

Fig. 3a) gives the semilog plot of the results of fig. 3. One sees that the radiolysis of the formate follows a zero order kinetics, while the destruction of the radiolysis products follows a first order kinetics. The two reaction

constants are calculated to be

$$k_o = 5 \times 10^{-4} \text{ mEq ml}^{-1} \text{ sec}^{-1}$$
$$k_1 = 6.7 \times 10^{-4} \text{ sec}^{-1}.$$

For a 0.5 M solution of sodium formate there is only linearity obtained up to app. 30% total conversion of the starting formate (fig. 5) between the reductant formation and total energy absorbed. This reductant concentration titratable in acid solution (2nd R_a-value) corresponds to an energy absorption of app. 90×10^6 rads. The maximum of the titration curve for the 0.5 M solution of sodium formate is finally reached after app. 43% conversion for the 1st R_a-value and after app. 48% conversion for the 2nd R_a-value. The 5% difference between these two values represents an absolute minimum of reducing compounds formed besides of oxalate. The concentration of reductants being oxidized in acid solution decreases after 180×10^6 rads absorption.

4.1.2 - PERMANGANATE TITRATION OF REDUCTANTS IN ALKALINE SOLUTION

In alkaline solution not only oxalate but also formate and anions of higher carboxylic acids are oxidized by potassium permanganate. At least up to about 250 Mrad absorption no linearity between the titration values and the dose absorbed is obtained (fig. 5).

4.2 - DETERMINATION OF CARBOXY GROUPS BEING DESTROYED DURING RADIOLYSIS AND TRANSFORMED INTO CARBON DIOXIDE AND NEUTRAL SUBSTITUENTS, RESPECTIVELY

From the data obtained for the total hydroxide and for the free hydroxide in the irradiated solution (table 3) the equivalents of carbon dioxide being formed during the radiolysis and the equivalents of carboxy groups being transformed into neutral substituents can be calculated:

H_t represents the total number of equivalents of - COOH groups being destroyed by the radiolysis. The number of carboxy groups still present in the solution is then

$$n\ (-\ COOH) = c_o - H_t \quad (mEq/50\ ml)$$

c_o = initial formate concentration

The difference between the H_t and the H_f-values is due to the presence of carbon dioxide. Because of H_2CO_3 being a dibasic acid the number of mMoles CO_2 being formed in the solution and being present as CO_3'', HCO_3', H_2CO_3 or CO_2 is accordingly:

$$n\ (CO_2) = \frac{H_t - H_f}{2} \qquad (mEq/50\ ml)$$

The number of mEq of neutral substituents being formed from carboxy groups is then:

$$\begin{aligned} n(c_{neutral}) &= c_o - n(COOH) - n(CO_2) \\ &= c_o - (c_o - H_t) - n(CO_2) \\ &= H_t - n(CO_2) \\ &= H_t - \frac{H_t - H_f}{2} \\ &= \frac{H_t + H_f}{2} \end{aligned}$$

The calculated values for the formation of carbon dioxide and of neutral substituents originating from the carboxy groups of sodium formate during the radiolysis are listed in table 6.

TABLE 6 RADIOLYSIS OF o.5 N SODIUM FORMATE
DISAPPEARANCE OF -COOH AND FORMATION OF CO_2
AND NEUTRAL SUBSTITUENTS

IRRADIATION TIME (sec)	TOTAL DOSE (10^6 rads)	n(-COOH)	n(CO_2)	n(C-neutral)
		(mEq / 5o ml)		
o	o	25.o	o.oo	o.oo
37.5		24.7	o.o8	o.23
15o	25	23.2	o.49	o.28
3oo	5o	21.5	1.o1	2.46
45o	75	19.2	1.98	3.82
6oo	1oo	17.3	2.71	4.98
75o	125	15.7	3.3	6.o
9oo	15o	14.3	4.1	6.6
1o5o	175	13.5	4.8	6.7
12oo	2oo	13.o	5.8	6.2
15oo	25o	11.7	8.1	5.2
21oo	35o	9.3	12.4	3.3

The kinetics for the disappearance of the total amount of carboxy groups are graphically illustrated in fig. 9. From the beginning of the radiolysis up to 15o x 10^6 rad absorption a linear relationship is observed when comparing the total dose absorbed and the amount of COOH disappeared. At higher energy absorptions decreasing amounts of carboxy groups are destroyed by the radiolysis.

Fig. 9 shows also that up to the same value of 150×10^6 rad energy absorption the increase in carbon dioxide and neutral substituents is proportional to the total dose absorbed. After that value for the energy absorption there appears therefore a break point for all three curves, indicating at higher energy absorptions a slightly slower rate of destruction of carboxy groups, a strongly decreasing rate of formation of neutral substituents and a somewhat higher rate of formation of carbon dioxide.

After 150×10^6 rad absorption also the reductant formation shows a maximum (fig. 5). This leads to the conclusion that after 150×10^6 rad energy absorption most of the initially present formate molecules have undergone complete destruction. The concentration of the more radiation stable oxalate, tartronate and of other acid anions is then approaching a maximum and therefore a decreased rate for the disappearance of carboxy groups results. But also the neutral substituents, being formerly produced by the formate decomposition are now formed at a lower rate and their decomposition exceeds their rate of formation. An increased rate of carbon dioxide formation results.

4.3 - PRODUCT FORMATION

The initially present carboxy groups of sodium formate in aqueous solution would finally be quantitatively transformed into molecular carbon dioxide and water. This can be done directly or via molecular transients being in their oxydational state between initial and end products. These intermediates can be carbonyl compounds, primary, secondary or tertiary alcohols or molecules containing alkyl groups. To each of these molecular species a reduction equivalent (S-value)

and an equivalent weight can be assigned. In table 7 are listed the group weights, reduction equivalents and the equivalent weights of all expected functional groups, being initially present or being formed as reducing intermediates during prolonged radiolysis.

The reduction equivalent is hereby determined in the following way:

If the formula of the functional group is $C_mO_nH_p$ we write the reaction:

$$C_mO_nH_p + rO = mCO_2 + \frac{1}{2} p\ H_2O$$

where $r = 2m + \frac{1}{2} p - n$.

Then $2r = 4m + p - 2n$ is the value of the reduction equivalent.

TABLE 7 REDUCING FUNCTIONAL GROUPS OF AQUEOUS FORMATE RADIOLYSIS

FUNCTIONAL GROUP	MOLECULAR WEIGHT	REDUCTION EQUIVALENT (S-value)	EQUIVALENT WEIGHT
-COOH	45	1	45
HCOOH	46	2	23
=CO	28	2	14
=COH	29	3	9,7
-CHO	29	3	9,7
=CHOH	3o	4	7,5
$-CH_2OH$	31	5	6,2
$=CH_2$	14	6	2,7

The permanganate oxidation in alkaline medium of the radiolyzed solution leads to the determination of all reducible substituents (R_b-value).

After the complete disappearance of starting formate (reduction equivalent 2) in the solution when only carboxy groups with a reduction equivalent 1 are present, the following equation holds

$$R_b = S\ (\text{-COOH}) \cdot n\ (\text{-COOH}) + S_{neutral} \cdot n\ (\text{C-neutral})$$

$$S_{neutral} = \frac{R_b - n\ (\text{-COOH})}{n\ (\text{neutral})}$$

$S\ (\text{-CO}_2\text{H})$	number of reduction equivalents of -COOH groups (=1)
$n\ (\text{-COOH})$	number of moles of -COOH-groups
$S_{neutral}$	average number of reduction equivalents of all neutral groups
$n\ (\text{C-neutral})$	number of moles of neutral C-functions.

The calculated S_n-values,*) i.e. the number of permanganate equivalents used for the reduction of neutral substituents in the radiolyzed solution have been calculated for each point of the radiolysis. The values are listed in table 8 and graphically illustrated in fig. 10.

*) For brevity we write from now on S_n instead of $S_{neutral}$.

TABLE 8 S_n-VALUES OF NEUTRAL REACTION PRODUCTS

IRRADIATION TIME (sec)	TOTAL DOSE (10^6 rad)	$S_{neutral}$-VALUE
150	25	16.5
300	50	8.05
450	75	4.75
600	100	3.5
750	125	2.67
900	150	2.34
1050	175	2.19
1200	200	2.12
1500	250	2.21
2100	350	2.40

Only after 900 seconds irradiation time and 150 x 10^6 rads absorption "realistic" S_n-values are reached. This is in agreement with the observation, that only after this absorption negligible amounts of formate are present in the irradiated sodium formate solution. It is nevertheless possible to extrapolate the number of reduction equivalents also for shorter irradiation times as shown graphically in fig. 10. At zero absorptions the number of reduction equivalents approaches a value of 2, which is the reduction equivalent for formic acid. After app. 1200 sec irradiation time (240 x 10^6 rad absorption) 2,12 reduction equivalents are necessary for oxidizing the solution. This value increases to 2,2 after 2500 sec irradiation time (300 x 10^6 rad absorption). This is a rough indication that at this point not more than 20% compounds with a reduction equivalent of 3 (e.g. tertiary alcohols), or 10% compounds with a reduction equivalent of 4 (e.g. secondary alcohols), or 6% of compounds with a reduction equivalent of 5 (e.g. primary alcohols) or 5% compounds with a reduction equivalent of 6 (e.g. compounds containing a methylene group) are present.

4.3.1 - FORMATE DECREASE

A rough estimation of the formate concentration in the irradiated samples can be made by the following two approaches:

a) From the acid titrations the number of acid equivalents (n(COOH)) is known. They include both the equivalents of formic acid and all other carboxylic acids. From the permanganate titrations in alkaline solution the number of reduction equivalents R_b has been determined. They include those necessary for reducing formic acid (reduction equivalent 2), all other carboxylic acids (reduction equivalent 1) and neutral substituents (reduction equivalent S_N, to be determined from fig. 10). The reduction equivalents necessary for the oxidation of formic acid and all other carboxylic acids can be determined by substracting from the R_b-value the reduction equivalents necessary for the oxidation of neutral substituents:

$$R_b - S_n n(C_{neutral})$$

From the fact that 2 reduction equivalents are needed for the formate oxidation and 1 reduction equivalent for the oxidation of all other carboxylic acids the following equations can be derived:

$$R_b - S_n \cdot n\ (C_{neutral}) = n\ (COOH) + n\ (formate)$$

$$n\ (formate) = R_b - S_n \cdot n\ (C\ neutral) - n\ (-COOH).$$

The values obtained for the formate present after different irradiation times are listed in table 9.

TABLE 9 FORMATE CONCENTRATIONS AFTER RADIOLYSIS OF o.5 n SODIUM FORMATE SOLUTIONS

IRRADIATION TIME (sec)	TOTAL DOSE (10^6 rad)	FORMATE CONCENTRATION (mM /5o ml solution)
0	0	25
15o	25	18.6
3oo	5o	14.9
45o	75	1o.3
6oo	1oo	6.9
75o	125	3.3
9oo	15o	1.1
1o5o	175	o.1
12oo	2oo	0
15oo	25o	0
21oo	25o	o.1

b) As observed in fig. 9 the decrease of the sum of carboxy groups (-COOH) being titrated in the radiolyzed solutions shows a strong retardation after 15o x 10^6 rad absorption. This was explained (chapter 4.2) on the basis that at this point most of the initially present formate has undergone complete destruction. Only carboxy groups of reaction products, being more slowly decomposed, are then present. A complete formation curve of carboxy group containing compounds can be very roughly graphically extrapolated to zero as outlined in fig. 11. The difference between the total of carboxy groups and the carboxy groups from consecutive reaction products would then represent the concentration of formate carboxy groups.

The values of carboxy concentrations from formate present are listed in table 10 and agree well with the values of table 9.

TABLE 10 FORMATE CONCENTRATIONS AFTER RADIOLYSIS OF 0.5 n SODIUM FORMATE SOLUTIONS

IRRADIATION TIME (sec)	TOTAL DOSE (10^6 rad)	FORMATE CONCENTRATION (mM/50 ml solution)
0	0	25
150	25	19.9
300	50	15.2
450	75	11.0
600	100	7.2
750	125	3.9
900	150	1.4
1050	175	0.0

c) Formate is only oxidized by potassium permanganate in alkaline and not in acid solution. Due to the fact that formate consumes two equivalents $KMnO_4$ per mole half the difference between the R_b and the R_a-values should represent the formate concentration. This value has to be corrected because during the irradiation also reaction products are formed in the irradiated solution, which are oxidized in alkaline but not in acid solution. After 150 x 10^6 rad absorption (complete formate destruction) 4.2 mEq of these reaction products are present. We assumed that the formation of these unknown compounds follows a linear relationship being zero at zero irradiation times and 4.2 mEq after 1050 sec irradiation time and corrected the difference between the R_b and R_a-values with an according value.

The values of carboxy concentrations from formate are listed in table 11.

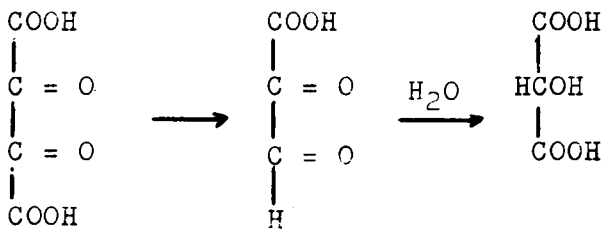
TABLE 11 FORMATE CONCENTRATION AFTER RADIOLYSIS OF 0.5 n SODIUM FORMATE SOLUTION

IRRADIATION TIME (sec)	TOTAL DOSE (10^6 rad)	FORMATE CONCENTRATION (mM/50 ml solution)
0	0	25
150	25	19.2
300	50	15.0
450	75	10.1
600	100	6.6
750	125	3.1
900	150	1.0
1050	175	0.05

The results of these three determinations of the formate concentration during the radiolysis of 0.5 N sodium formate solutions are graphically illustrated in fig. 12.

4.3.2 - FORMATION OF ACIDIC REACTION PRODUCTS

Our results and the results obtained by previous workers indicate the presence of at least three main products in the irradiated sodium formate solutions: formate, oxalate, and tatronate. The formation of the latter can occur via the formation of dioxoglutaric acid as initial product, which in an intramolecular Cannizzaro reaction forms tatronic acid.



Of these three main components formate is oxidized by permanganate only in alkaline solution, oxalate and dioxoglutarate in both acid and alkaline solution.

4,3.3 - G-VALUES OF PRODUCT FORMATIONS FROM A o.5 n SODIUM FORMATE SOLUTION

Our results allow the assignment of G-values for the formation of permanganate oxidizable compounds in acid solution (R_a), free hydrogen (H_f), total hydrogen (H_t), neutral substituents (C-neutral) and oxalate and for the decrease of permanganate oxidizable compounds in alkaline solution (R_b), carboxy groups and formate, as listed in table 13.

TABLE 13 G-VALUES OF PRODUCT FORMATION AND DISAPPEARANCE DURING THE RADIOLYSIS OF 0.5 n SODIUM FORMATE SOLUTIONS*)

G-VALUE formation resp. decrease	G-VALUE C-atoms/100 eV
1st R_a	+ 3.26
2nd R_a	+ 3.40
R_b	- 3.16
H_f	+ 0.5
H_t	+ 1.2
n(C-neutral)	+ 0.8
n(-COOH)	- 1.2
n(formate)	- 3.3
n(oxalate)	+ 2.2

*) the G-values are extrapolated for zero irradiation times

A C K N O W L E D G E M E N T

The authors take pleasure in acknowledging the help of Mr. Fred Dorpema in the design of the experimental equipment and in performing the Van de Graaff irradiations. We also thank Dr. H. Hannaert for his interest in this study and for valuable discussions.

LITERATURE

1) T.J.Hardwick, W.S.Guentner
J.Phys.Chem. 63 (1959) 896.

2) H.Fricke, E.J.Hart
J.Chem.Phys. 2 (1934) 824

3) E.J.Hart
J.Am.Chem.Soc. 73 (1951) 68

4) E.J.Hart
J.Phys.Chem. 56 (1952) 524

5) E.J.Hart
J.Am.Chem.Soc. 76 (1954) 4198

6) E.J.Hart
J.Am.Chem.Soc. 76 (1954) 4312

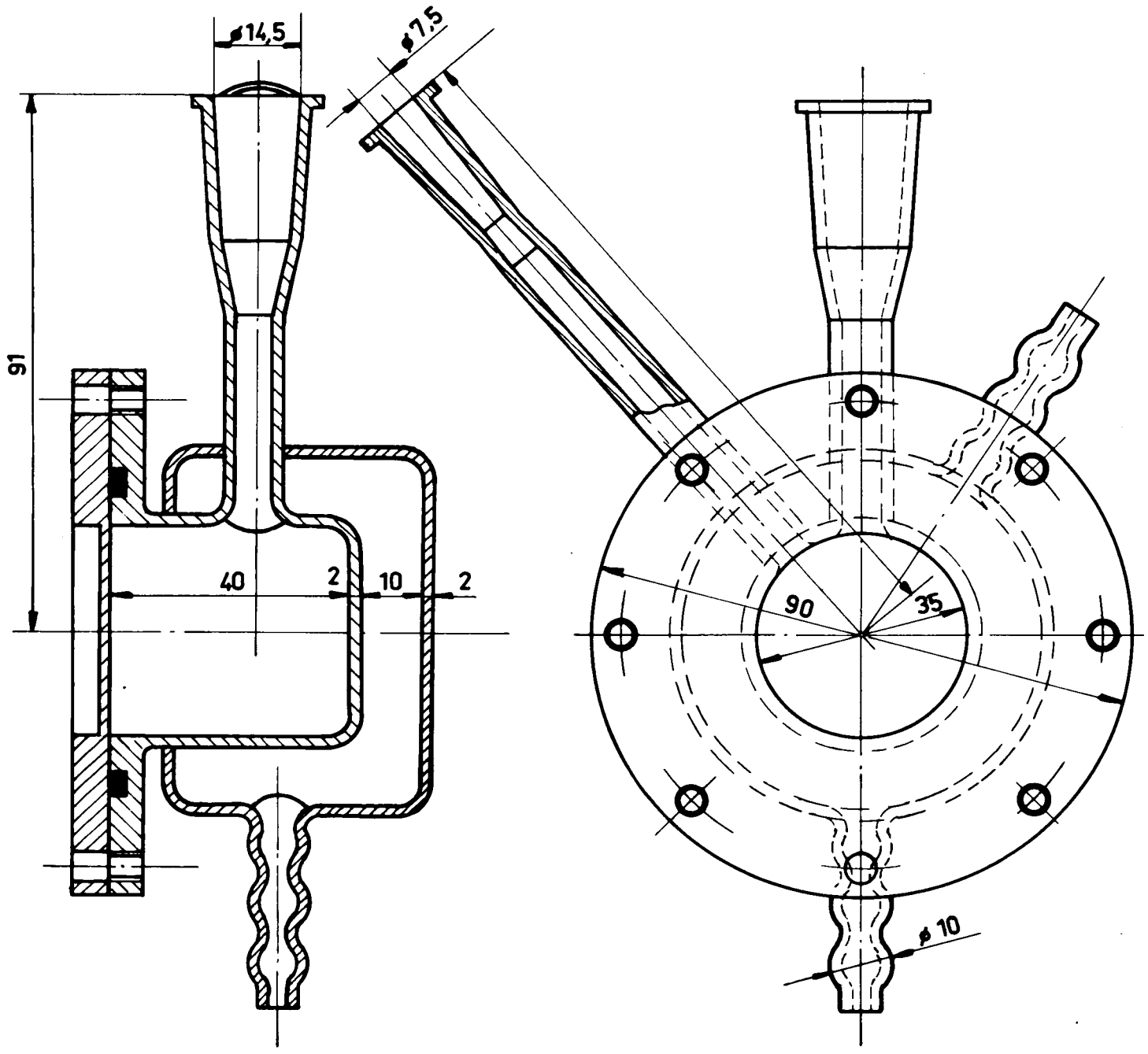
7) W.M.Garrison, W.Bennet, S.Cole
Rad.Res. 9 (1958) 647

8) E.Hayon, J.Weiss
Proc.2nd Intern.Conf. on the Peaceful Uses of Atomic Energy 29 (1958)

9) I.Janowsky, B.Bartonicek, J.Bednar
Collection Czech.Chem.Commun 28 (1963) 2245

10) T.J.Hardwick
Radiation Research 12, 5 (1960)

Fig. 1



IRRADIATION VESSEL (STAINLESS STEEL)

SCALE 1:1

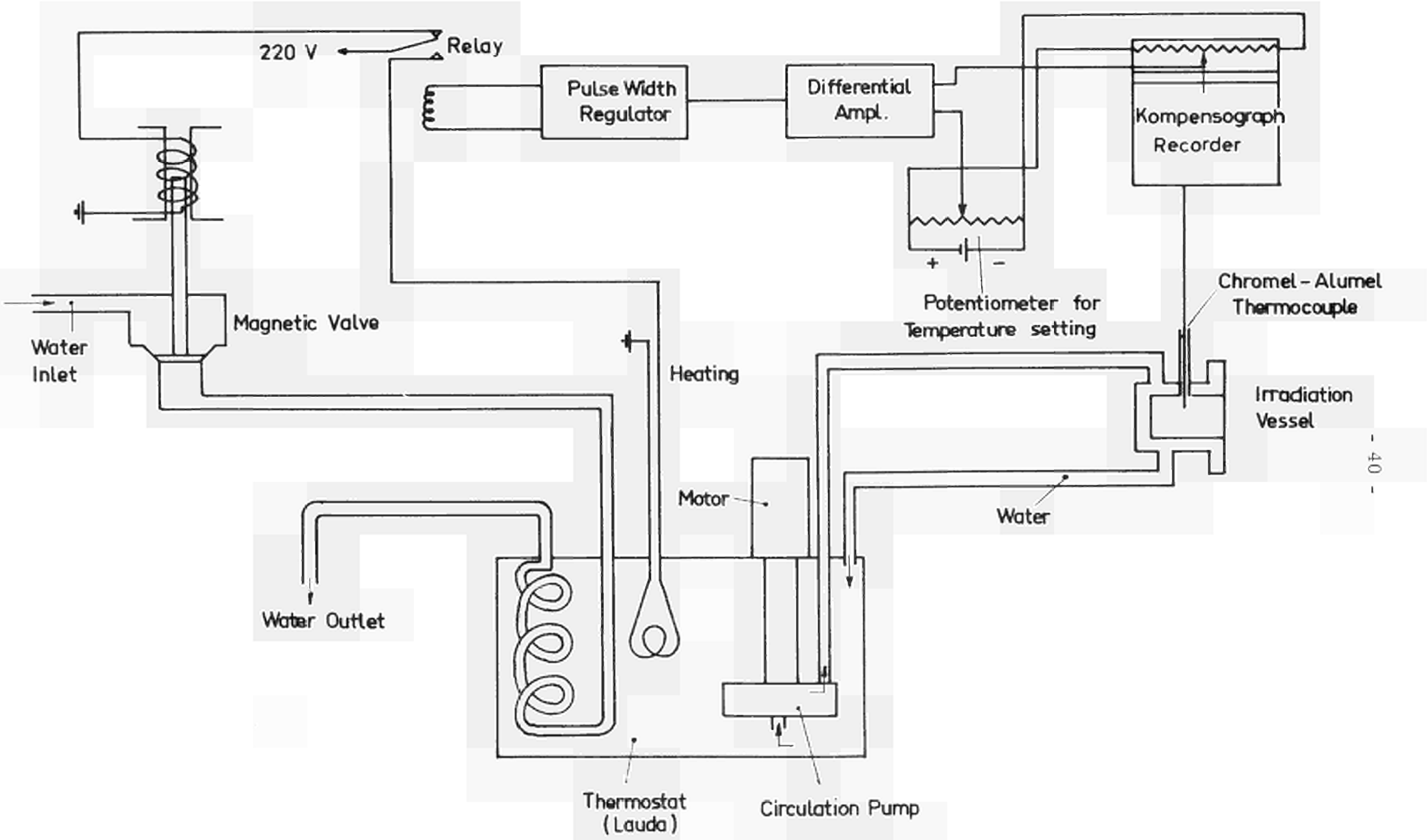


Fig. 2 TEMPERATURE CONTROL OF IRRADIATION VESSELS (30°–90°)

Fig. 3

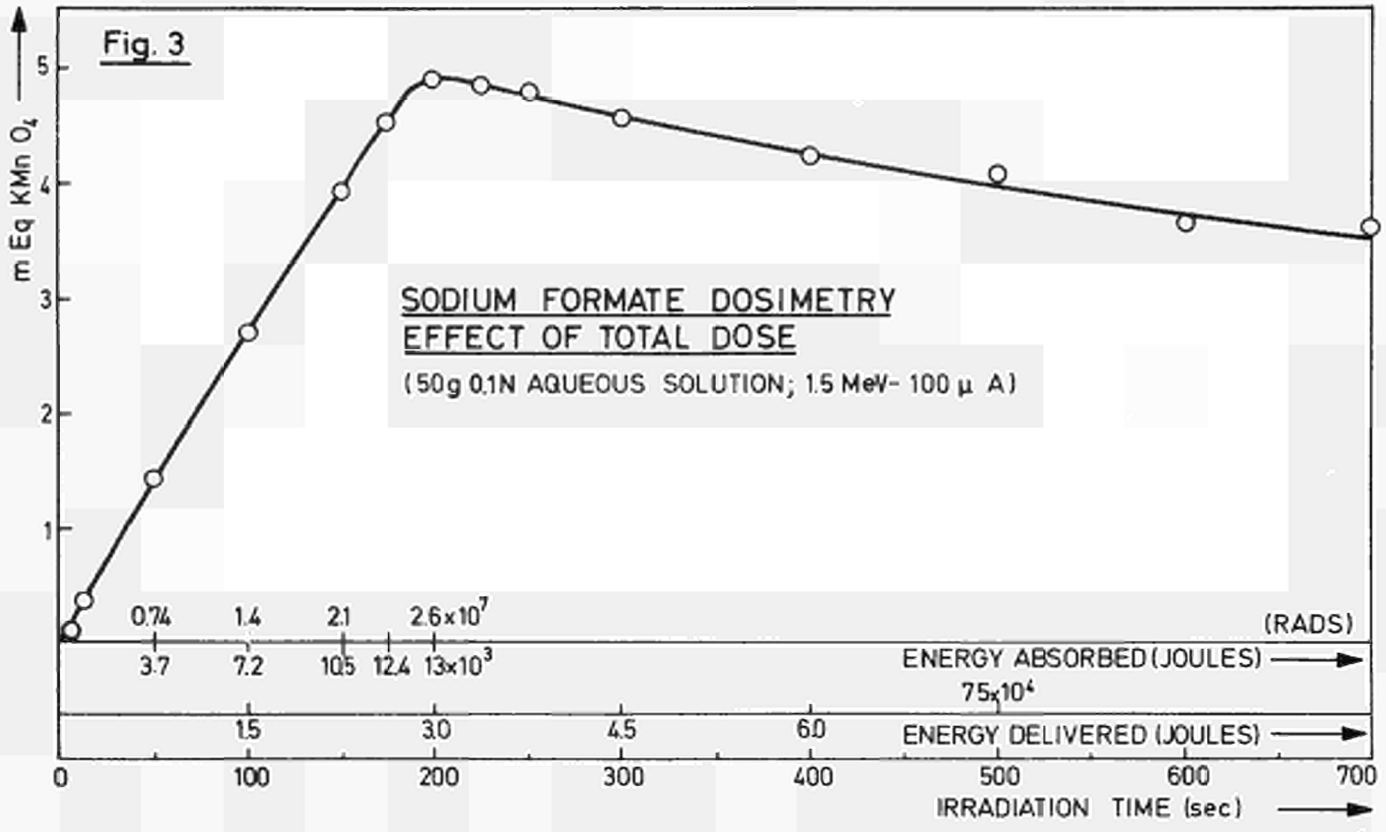

m Eq KMn O4
SODIUM FORMATE DOSIMETRY
EFFECT OF TOTAL DOSE
(50g 0.1N AQUEOUS SOLUTION; 1.5 MeV- 100 μ A)
0.74 1.4 2.1 2.6x10^7 (RADS)
3.7 7.2 10.5 12.4 13x10^3
ENERGY ABSORBED (JOULES)
75x10^4
1.5 3.0 4.5 6.0
ENERGY DELIVERED (JOULES)
0 100 200 300 400 500 600 700
IRRADIATION TIME (sec)

Fig. 3a

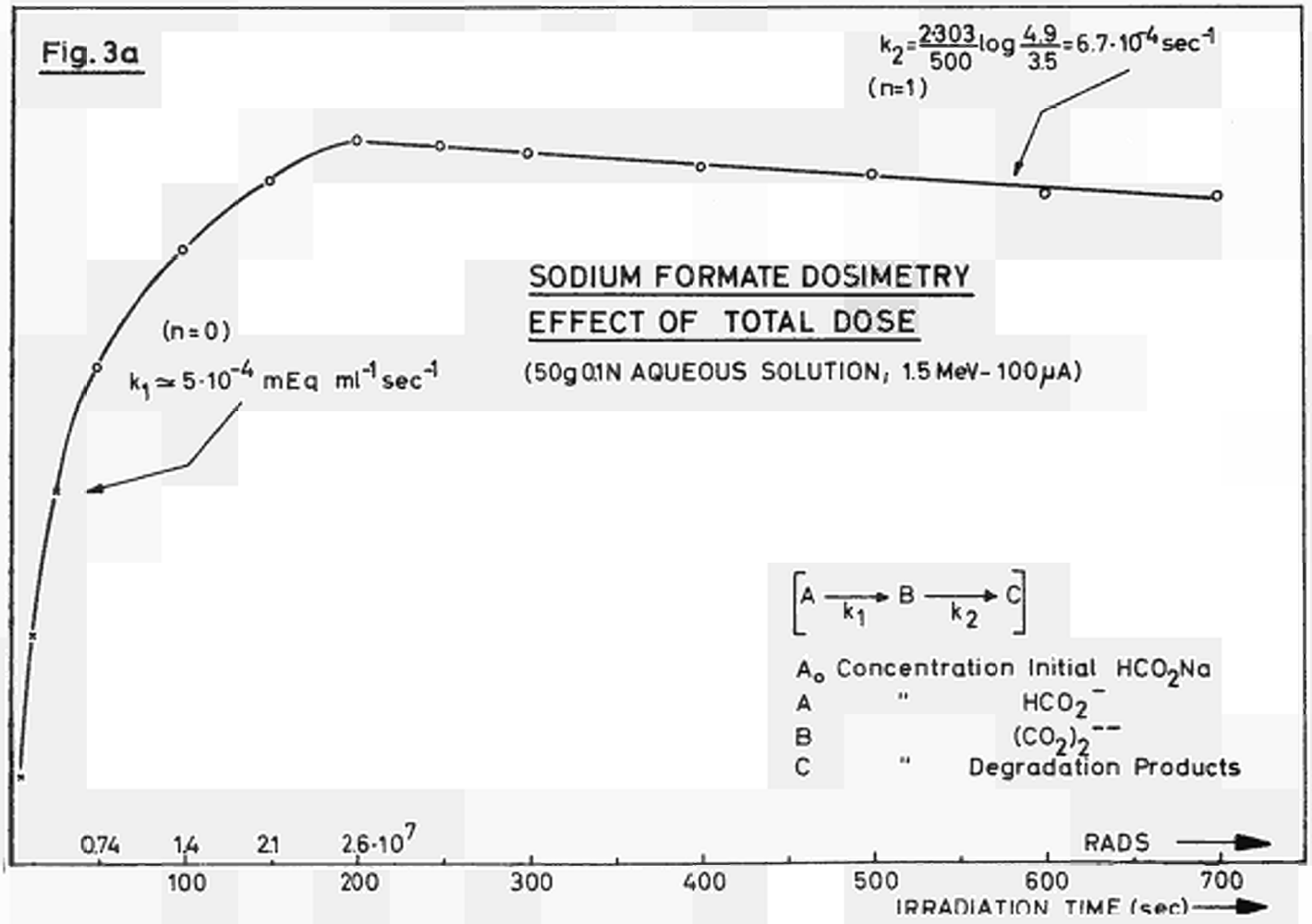

k2 = 2.303/500 log 4.9/3.5 = 6.7·10^-4 sec^-1
(n=1)
SODIUM FORMATE DOSIMETRY
EFFECT OF TOTAL DOSE
(50g 0.1N AQUEOUS SOLUTION; 1.5 MeV- 100 μA)
(n=0)
k1 ≃ 5·10^-4 mEq ml^-1 sec^-1
[A → B → C]
k1 k2
Ao Concentration Initial HCO2Na
A " HCO2^-
B (CO2)2^--
C " Degradation Products
0.74 1.4 2.1 2.6·10^7 RADS
100 200 300 400 500 600 700
IRRADIATION TIME (sec)

Fig. 4

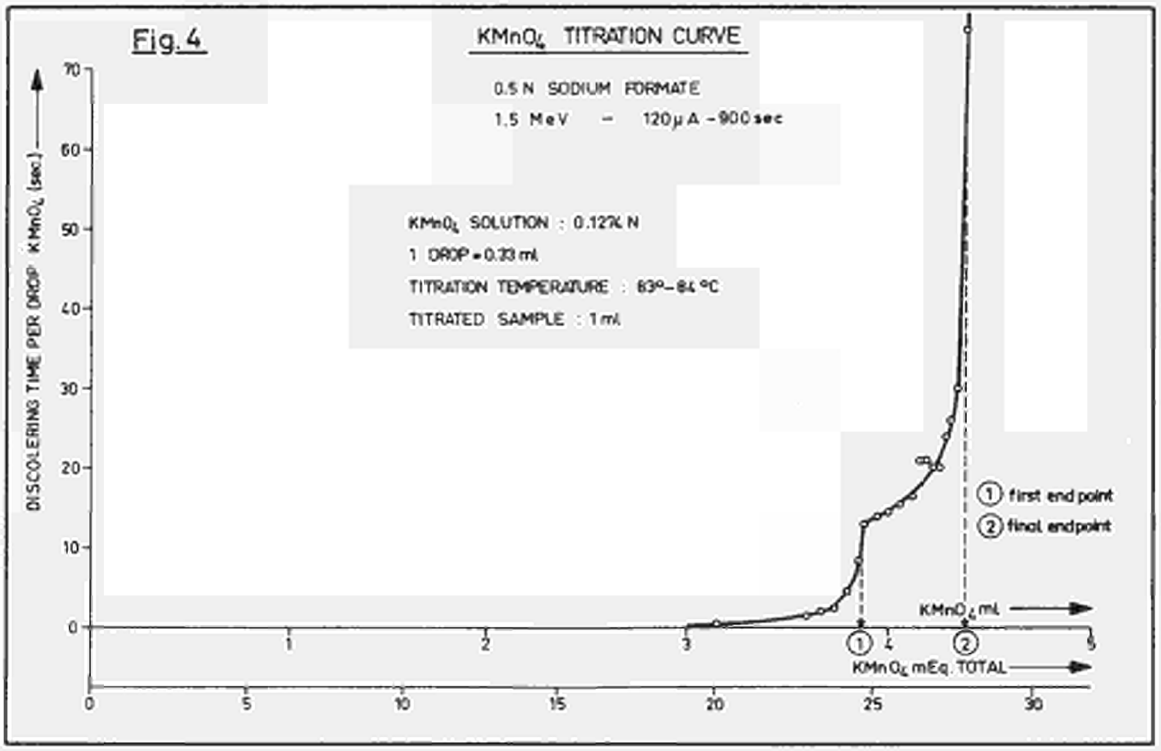

KMnO4 TITRATION CURVE
0.5 N SODIUM FORMATE
1.5 MeV – 120 µA – 900 sec
KMnO4 SOLUTION : 0.127 N
1 DROP = 0.03 ml
TITRATION TEMPERATURE : 83°–84 °C
TITRATED SAMPLE : 1 ml
DISCOLERING TIME PER DROP KMnO4 (sec)
1 first end point
2 final endpoint
KMnO4 ml
KMnO4 mEq. TOTAL

Fig. 5

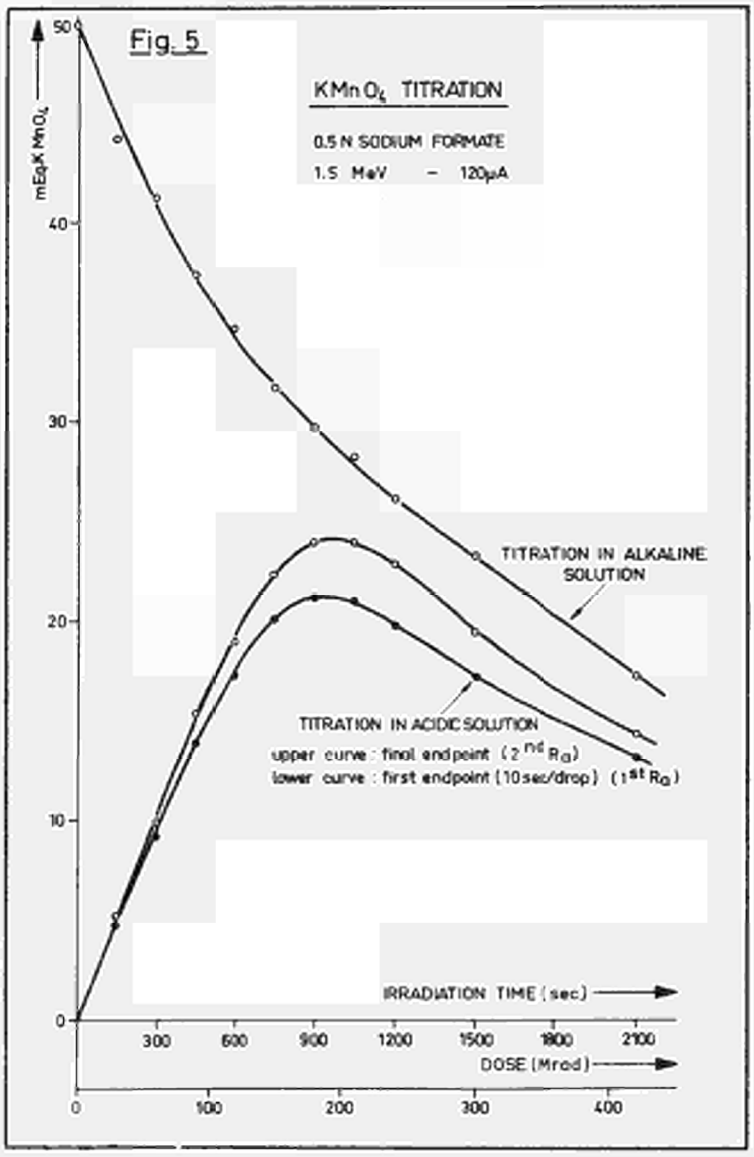

KMnO4 TITRATION
0.5 N SODIUM FORMATE
1.5 MeV – 120µA
mEq K MnO4
TITRATION IN ALKALINE SOLUTION
TITRATION IN ACIDIC SOLUTION
upper curve : final endpoint (2nd Rd)
lower curve : first endpoint (10 sec/drop) (1st Rd)
IRRADIATION TIME (sec)
DOSE (Mrad)

Fig. 6

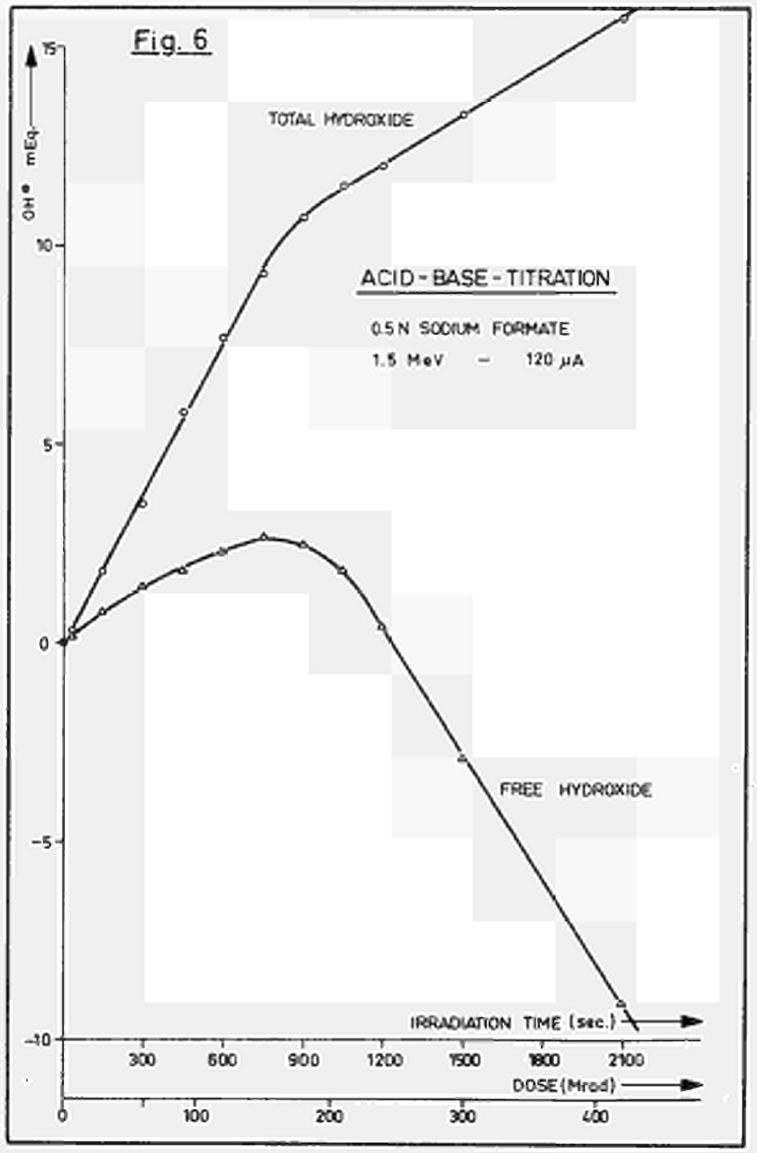
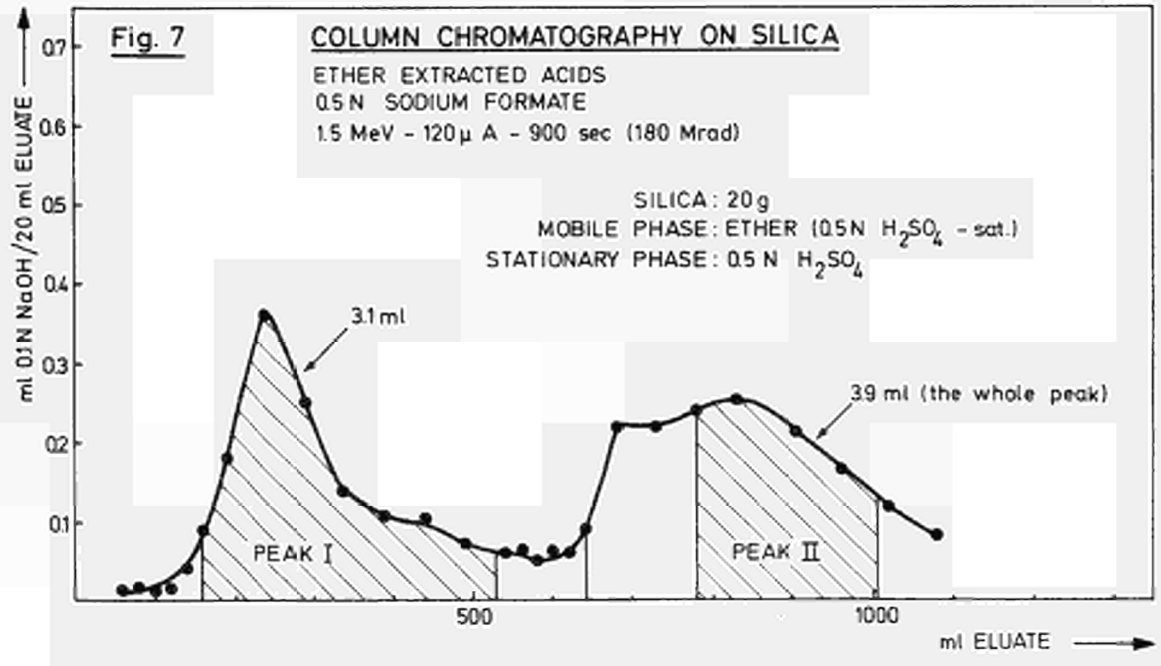

OH⊖ mEq
15
10
5
0
-5
-10
TOTAL HYDROXIDE
ACID - BASE - TITRATION
0.5 N SODIUM FORMATE
1.5 MeV – 120 μA
FREE HYDROXIDE
IRRADIATION TIME (sec.)
300
600
900
1200
1500
1800
2100
DOSE (Mrad)
0
100
200
300
400

Fig. 7


COLUMN CHROMATOGRAPHY ON SILICA
ETHER EXTRACTED ACIDS
0.5 N SODIUM FORMATE
1.5 MeV - 120 μ A - 900 sec (180 Mrad)
SILICA: 20 g
MOBILE PHASE: ETHER (0.5 N H_2SO_4 - sat.)
STATIONARY PHASE: 0.5 N H_2SO_4
ml 0.1 N NaOH/20 ml ELUATE
0.7
0.6
0.5
0.4
0.3
0.2
0.1
3.1 ml
3.9 ml (the whole peak)
PEAK I
PEAK II
500
1000
ml ELUATE

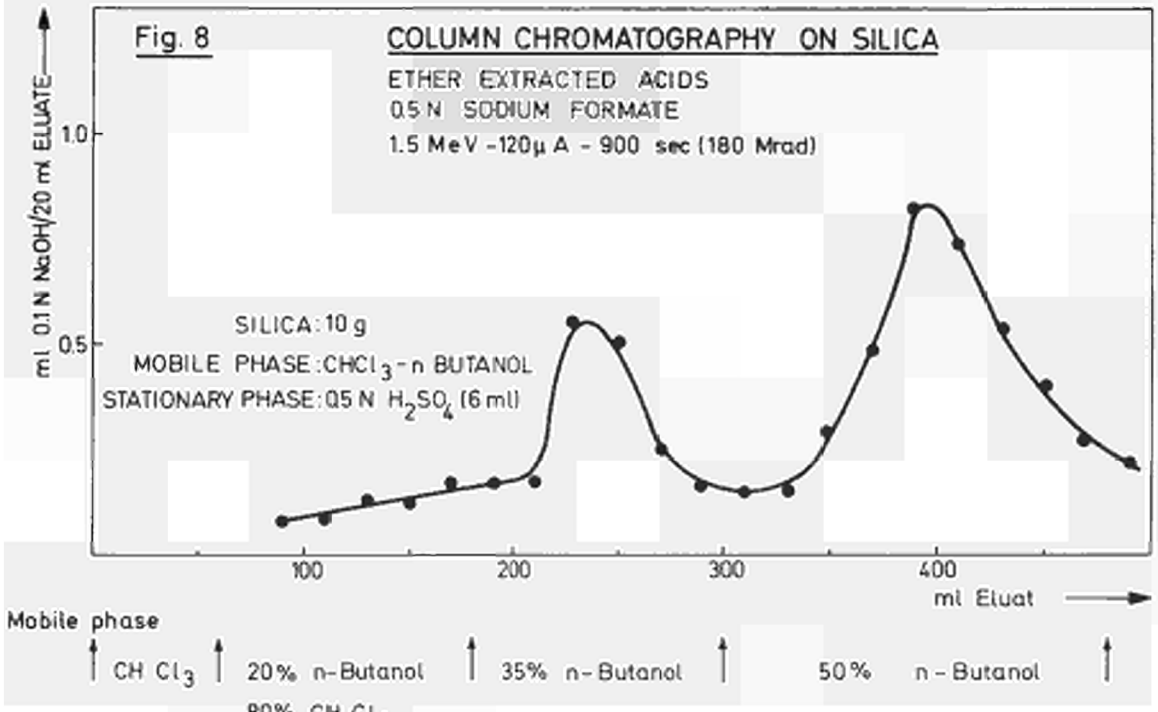


Fig. 8
COLUMN CHROMATOGRAPHY ON SILICA
ETHER EXTRACTED ACIDS
0.5 N SODIUM FORMATE
1.5 MeV -120μ A - 900 sec (180 Mrad)
ml 0.1 N NaOH/20 ml ELUATE
1.0
0.5
SILICA: 10 g
MOBILE PHASE: CHCl3 - n BUTANOL
STATIONARY PHASE: 0.5 N H2SO4 (6 ml)
100
200
300
400
ml Eluat
Mobile phase
CH Cl3
20% n-Butanol
80% CH Cl3
35% n-Butanol
50% n-Butanol

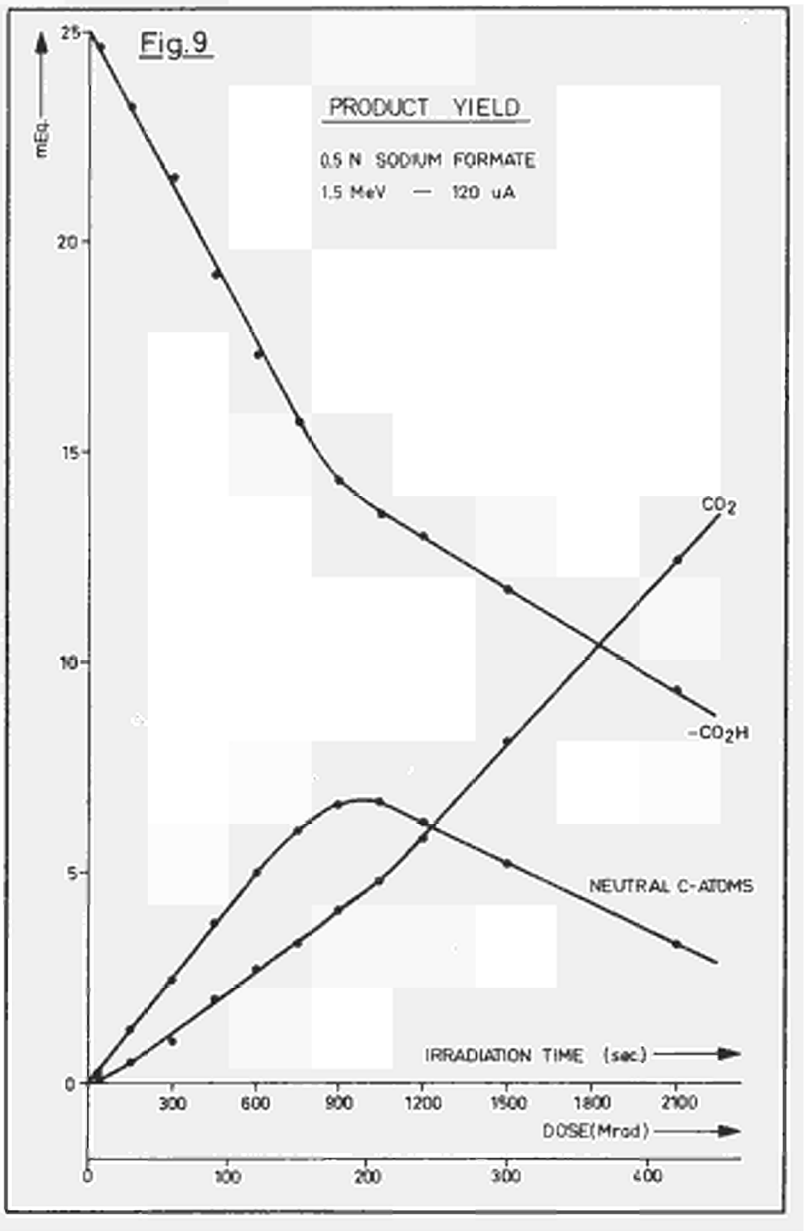


Fig. 9
PRODUCT YIELD
0.5 N SODIUM FORMATE
1.5 MeV — 120 uA
mEq.
25
20
15
10
5
0
CO2
-CO2H
NEUTRAL C-ATOMS
IRRADIATION TIME (sec.)
300
600
900
1200
1500
1800
2100
DOSE(Mrad)
0
100
200
300
400

Fig.10

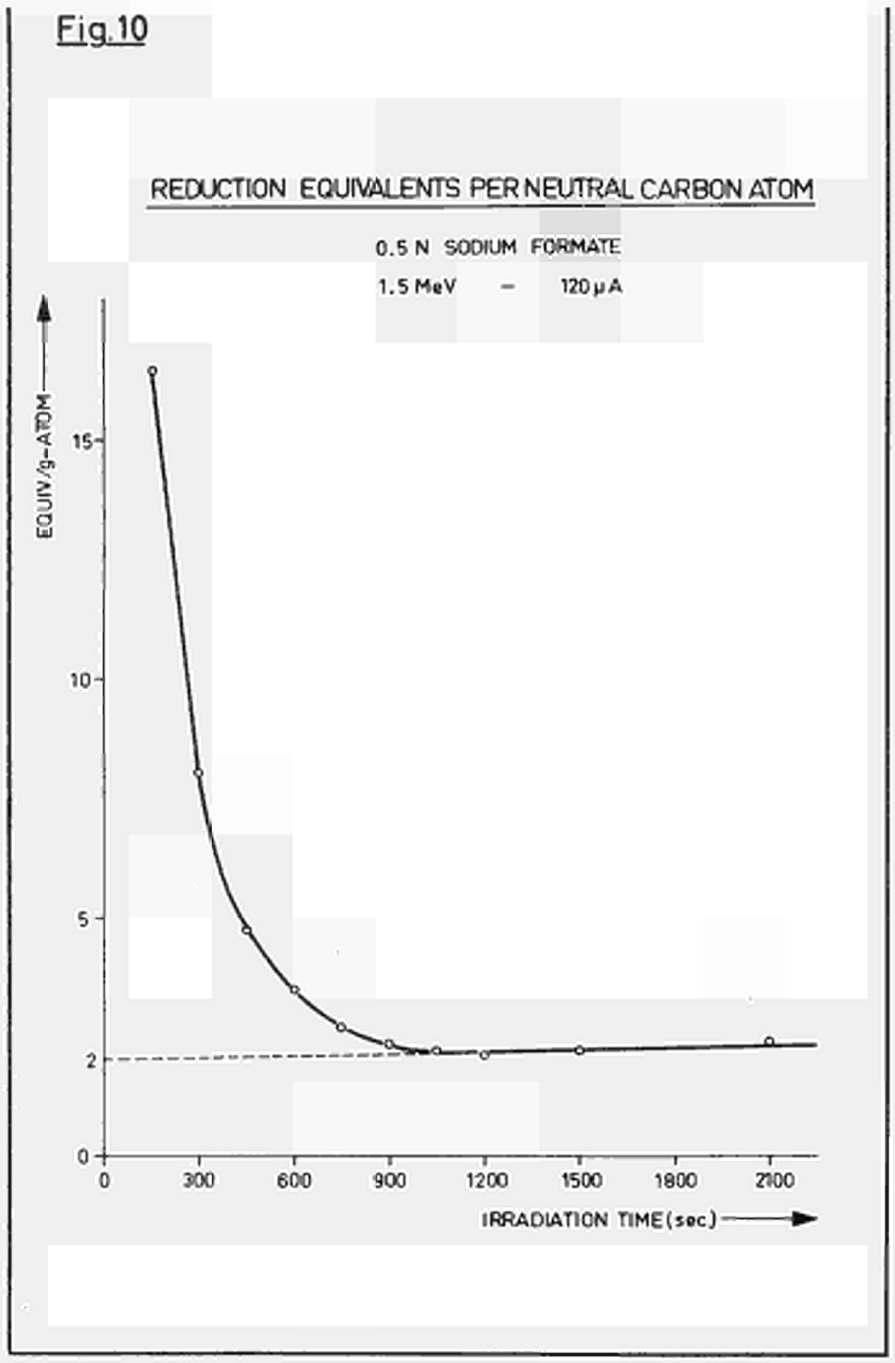
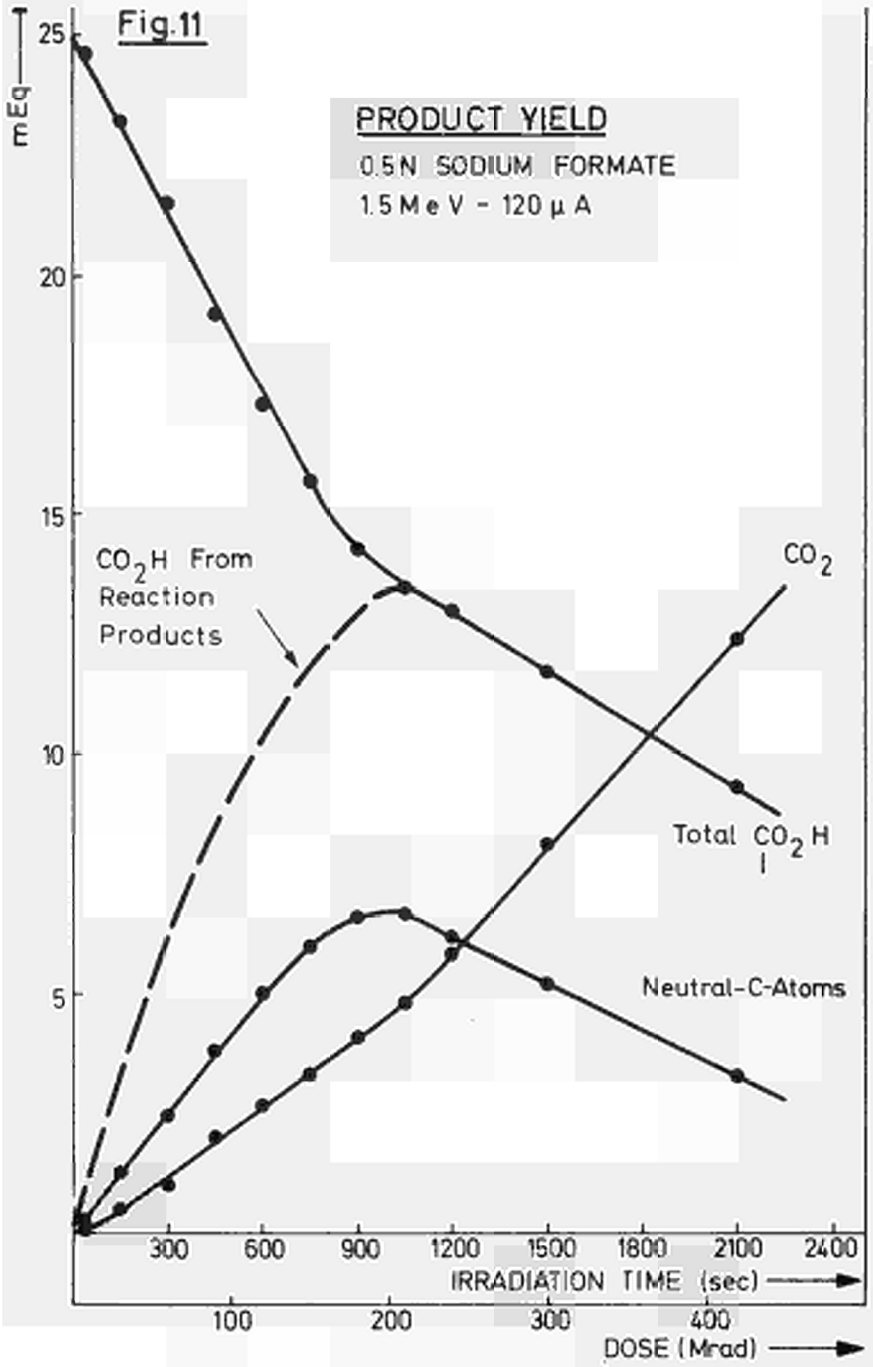

REDUCTION EQUIVALENTS PER NEUTRAL CARBON ATOM
0.5 N SODIUM FORMATE
1.5 MeV – 120 µA
EQUIV/g-ATOM
0
2
5
10
15
0
300
600
900
1200
1500
1800
2100
IRRADIATION TIME (sec)

Fig.11


PRODUCT YIELD
0.5 N SODIUM FORMATE
1.5 MeV - 120 µA
mEq
5
10
15
20
25
CO_2H From Reaction Products
CO_2
Total CO_2H
Neutral-C-Atoms
300
600
900
1200
1500
1800
2100
2400
IRRADIATION TIME (sec)
100
200
300
400
DOSE (Mrad)

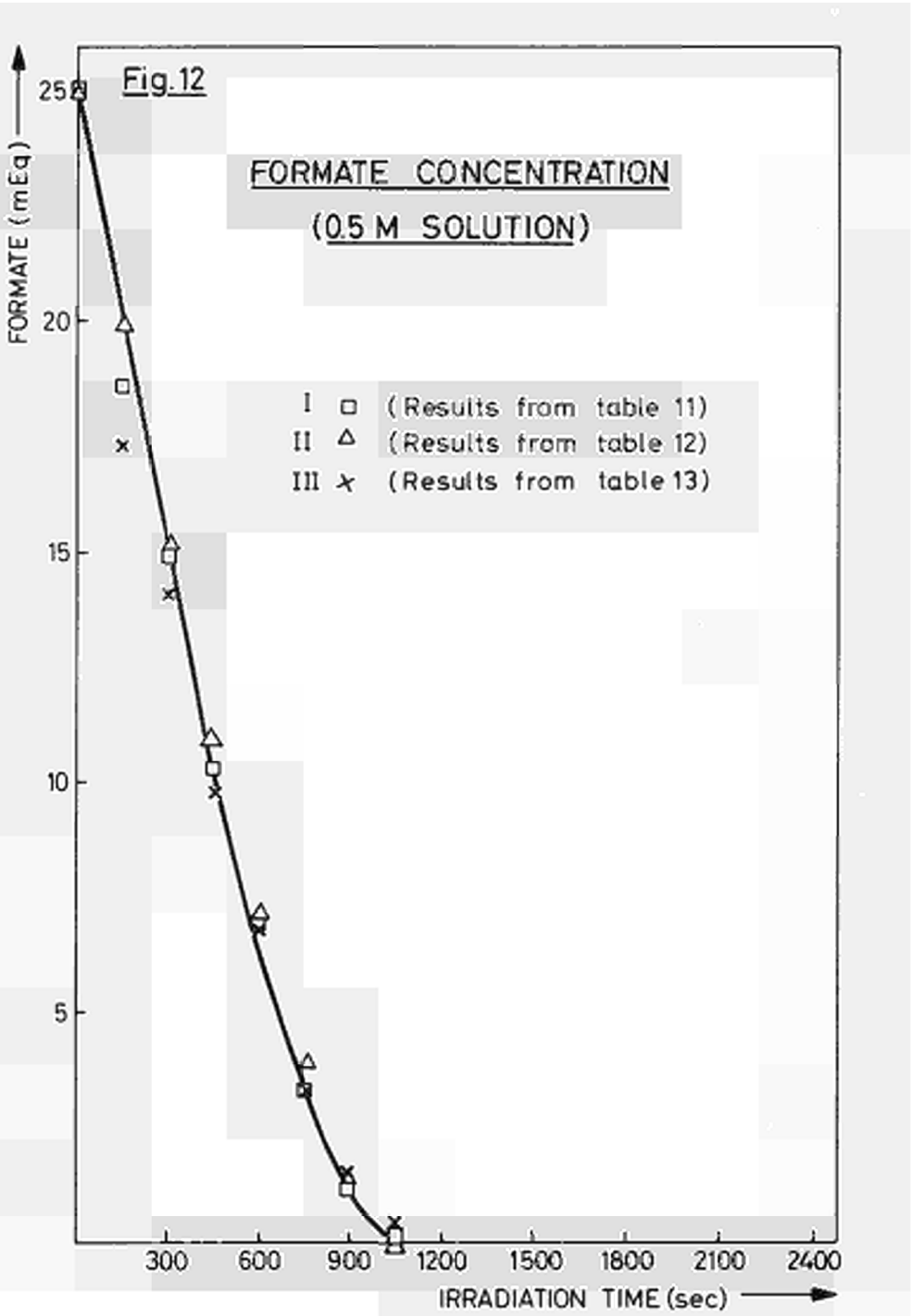
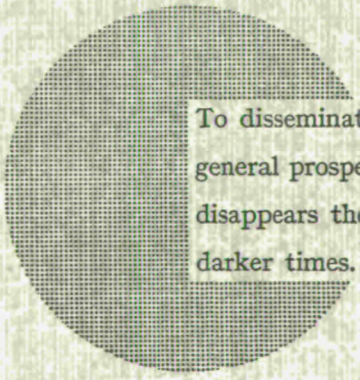


Fig.12
FORMATE CONCENTRATION
(0.5 M SOLUTION)
I □ (Results from table 11)
II △ (Results from table 12)
III × (Results from table 13)
FORMATE (mEq)
25
20
15
10
5
300
600
900
1200
1500
1800
2100
2400
IRRADIATION TIME (sec)



To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

SALES OFFICES

All Euratom reports are on sale at the offices listed below, at the prices given on the back of the front cover (when ordering, specify clearly the EUR number and the title of the report, which are shown on the front cover).

OFFICE CENTRAL DE VENTE DES PUBLICATIONS DES COMMUNAUTES EUROPEENNES
2, place de Metz, Luxembourg (Compte chèque postal Nº 191-90)

BELGIQUE — BELGIË
MONITEUR BELGE
40-42, rue de Louvain - Bruxelles
BELGISCH STAATSBLAD
Leuvenseweg 40-42, - Brussel

DEUTSCHLAND
BUNDESANZEIGER
Postfach - Köln 1

FRANCE
SERVICE DE VENTE EN FRANCE DES PUBLICATIONS DES COMMUNAUTES EUROPEENNES
26, rue Desaix - Paris 15e

ITALIA
LIBRERIA DELLO STATO
Piazza G. Verdi, 10 - Roma

LUXEMBOURG
OFFICE CENTRAL DE VENTE DES PUBLICATIONS DES COMMUNAUTES EUROPEENNES
9, rue Goethe - Luxembourg

NEDERLAND
STAATSDRUKKERIJ
Christoffel Plantijnstraat - Den Haag

UNITED KINGDOM
H. M. STATIONERY OFFICE
P. O. Box 569 - London S.E.1

EURATOM — C.I.D.
51-53, rue Belliard
Bruxelles (Belgique)